EIGHTH QUARTERLY R&D STATUS REPORT

Principal Investigator:
Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania

REPORTING PERIOD: 7/1/88 - 9/30/88

UNIVERSITY *of* PENNSYLVANIA

PHILADELPHIA, PENNSYLVANIA 19104

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SHORT TITLE OF WORK: **Conducting Electronic Polymers by Non-Redox Processes**

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per call J.C.

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   (b) Department of Materials Science (G.C. Farrington)

2. The Ohio State University
   Department of Physics (A.J. Epstein)

3. Lockheed Advanced Aeronautics Corporation
   Aeronautics Systems Group Research (T.S. Kuan)

4. Rensselaer Polytechnic Institute
   Department of Chemistry (G.E. Wnek)

5. University of Rhode Island
   Department of Chemistry (S.C. Yang)

6. Montclair State College
   Department of Chemistry (B.D. Humphrey)

*Financial information for each group given in Section IX.

II. Description of Progress

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)‡

(i) Summary of Progress

Polyaniline Fibers*

Exhaustive extraction of the emeraldine base form of polyaniline $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N=(C_6H_4)=N-]_x$ first by THF and then by NMP results in an ~83% yield of analytically pure emeraldine base which upon protonic acid doping with HCl gives a conductivity of ~18 S/cm. The NMP extract has a maximum molecular weight (g.p.c.) of ~325,000. Crystalline fibers (~25 - 50 μm) of emeraldine base or emeraldine•HCl can be formed by drawing fibers of emeraldine base in a water/NMP solution or in aqueous HCl respectively. Scanning electron micrographs show they possess a clean, smooth, even surface. Conductivities in the range 30-80 S/cm are obtained for the emeraldine•HCl fibers.

*Work supported in part by the URI and in part by the University of Pennsylvania.

Oriented Polyaniline Films*

Oriented polyaniline can be obtained by evaporating (in the presence of a heat lamp) a solution of emeraldine base $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N=(C_6H_4)=N-]_x$ in NMP on a polyethylene substrate while the substrate is being mechanically stretched. Small angle X-ray data indicate anisotropy in the electron density both parallel and perpendicular to the stretching direction. The anisotropy disappears for distances less than about 5 nm. The orientation of fibril-like structure is confirmed by scanning electron microscopy and is consistent with the result obtained on both emeraldine base and emeraldine•HCl by polarized infrared spectroscopy and polarized optical microscopy.

*Work supported in part by the URI and in part by NSF Grant No. DMR-85-19059.

‡In collaboration with Professor A.J. Epstein, Department of Physics, The Ohio State University.

Synthesis of Polyaniline in Preselected Oxidation States*

The base form of polyanilines, $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_y[-(C_6H_4)-N=(C_6H_4)=N-]_{1-y}$, can in principle exist in a variety of oxidation states ranging from the completely reduced polymer, (y=1), to the completely oxidized material (y=0). Polyaniline can be controllably synthesized in any predesignated, macroscopic oxidation state by chemical oxidation of the completely reduced form by O_2, H_2O_2, $SOCl_2$, $NOPF_6$, Cl_2, $FeCl_3$, $SnCl_4$, (m-Cl)$C_6H_4C(O)OOH$, $(NH_4)_2S_2O_8$, TCNQ, etc. In certain cases, e.g., O_2, the final oxidation state of the polymer is conveniently limited by the oxidation potential of the oxidizing agent. Extensive oxidation, $(1-y) \geq \sim 0.75$, results in complete or partial deprotonation to give ultimately the base form of the polymer in that given oxidation state. The use of H_2O_2 in aqueous acid, HA, is particularly useful since it has the potential of introducing a variety of different A^- dopant ions.
*Work supported in part by the URI and in part by the University of Pennsylvania.

(ii) Major Equipment Purchased or Constructed

A Perkin-Elmer Lambda-9 Series (UV/Vis/NIR) instrument was purchased.

b. Materials Science and Engineering (Farrington)

Ching-min Wu, Jonathan Foreman, and Rokeya Huq have completed a study of the electrochemical redox chemistry of oriented and ultra-pure poly(acetylene). In electrochemical terms, the material seems essentially equivalent to the Shirakawa material. It shows no sign of enhanced stability nor is it more promising as an electrode material for batteries. As a result, this phase of the investigation has ended.

Gary Jones has begun to use dynamic mechanical analysis in his studies of ion bonding and interaction in POE solutions containing multivalent cations. Again, the goal is to understand the factors that control the rate of ion motion in these materials.

2. The Ohio State University

Department of Physics (Epstein)‡

(i) Summary of Progress

In collaboration with J.P. Pouget (Université Paris-Sud, France) we have begun to reanalyze the x-ray diffraction data for emeraldine base and protonated emeraldine base that was acquired during the visit of A.J. Epstein to Université Paris-Sud in the fall of 1986. The emeraldine base material is essentially amorphous with only a small percentage crystallinity. Upon doping there is a conversion of the amorphous part into the crystalline one. This increase in crystallinity upon doping is dramatically different from the situation from polyacetylene, where doping decreases the crystallinity. Preliminary analysis of the results suggest that the Cl^- inserts in the zigzag of the polymer backbone. With increasing doping the parallel polymer chains are thus pushed further apart.

We have extended our photoinduced infrared absorption studies of emeraldine base polymer. These results show that polarons are formed upon optical pumping into the exciton absorption band near 2eV. We observe unusually weak photoinduced infrared active vibrational (IRAV) modes. These data contrast sharply with earlier studies of polyacetylene and polythiophene. Our results of polyaniline demonstrate the important role of this system's polarons with large mass, strong pinning and low mobility. An analysis of the photoinduced infrared modes in terms of the amplitude mode theory was mentioned in the last quarterly report. This analysis was carried out despite the presence of a large energy gap (~3.8 eV) in emeraldine base that may be thought of as originating primarily as a result of the π-π^* transitions involving the molecular orbitals of the benzene-like groups. In view of the large "extrinsic" gap in the emeraldine base, we have implemented an alternate approach to polaron formation emphasizing the role of the extrinsic (π-π^*) gap. One approach is that of bond-order polarons, developed by Rice and Phillpot and applied by them to tetrahedrally-bonded homopolymers (TBH) such as poly(organosilylene), which provides insight despite such important differences between the polyanilines and TBH as the "A-B" and charge conjugation asymmetric nature of the polyanilines. Assuming an energy gap 2Δ=3.8 eV, a

‡In collaboration with Professor A.G. MacDiarmid, Department of Chemistry, University of Pennsylvania.

valence bandwidth of 2=0.4 eV, a polaron decay length of order half the nitrogen-nitrogen spacing, and an electron-phonon interaction the same as that of polyacetylene, ~4.3 eV/Å, we obtain M_{pol} ~220m_e. The lower polaron energy level is calculated to be only δp ~0.5 eV above the valence band. Though clearly massive, the actual M_{pol} is very sensitive to the assumed value of the polaron decay length. For example, an increase in the decay length of 20% gives M_{pol} ~88m_e and δp ~0.3 eV. The bond-order polaron model is in agreement with observation of weak photoinduced IRAV modes that have low energy shoulders extending to ~0.9 times the photoinduced IR frequency. It is noted that the broad photoinduced absorption centered at ~1350 cm^{-1} may correspond to the pinned Goldstone mode of this system as expected for either the amplitude mode or bond-order models. Similarly, large values of M_{pol} can be obtained utilizing the Holstein polaron picture.

Optical absorbances in the photon energy range 1 to 6 eV were measured on thin films of the emeraldine base (EB) and emeraldine salt (ES) forms of polyaniline. The measured data were fitted to a classical oscillator model to obtain the optical constants. These fits reveal that the oscillator strength in the energy range studied is nearly identical for EB and ES, consistent with the basic model of protonic doping. The calculated real and imaginary parts of the refractive index are in agreement with limited earlier ellipsometric results. Estimates of oscillator strengths are in agreement with our assignments of excitons in EB and polarons in ES.

We have extended our transport studies of the new highly conducting forms of polyacetylene. Temperature dependent thermoelectric powered studies of heavily iodine-doped material showed a room temperature thermopower of ~ +10μ V/K and a linear temperature dependence, similar to AsF_5 doped S-$(CH)_x$. Magnetoresistance studies of N-$(CH)_x$ to field of 8 x 10^4 Gauss and low temperatures are nearly identical to earlier studies on S-$(CH)_x$. These results together with the magnetic susceptibility discussed in the previous quarter's report, show that the microscopic transport phenomena in highly doped N-$(CH)_x$ is actually similar to that within the S-$(CH)_x$. That is, the results indicate that the increased conductivity may be explained by the increase in the relaxation time along the chain or an interchain transfer that help avoid entrapment of the electrons within a single chain. This leads to a three-dimensional delocalization of electrons responsible for the higher conductivity. These results are in accord with new data on the ac conductivity of unoriented N-$(CH)_x$.

(ii) Major Equipment Purchased or Constructed

Miscellaneous supplies for current equipment maintenance and replacement were purchased including a fuel cell for the glove box; various optical components e.g. lamps, windows, optical mounts, and filters. A heat exchanger was purchased to provide cooling for the EPR instrument.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Summary of Progress

Mechanistic Studies of Aniline's Oxidative Polymerization

Conductive polyaniline emeraldine is commonly synthesized via the oxidative polymerization of aniline in aqueous hydrochloric acid using ammonium peroxydisulphate at reduced temperatures. The strong oxidant is needed to initiate the oxidation of aniline. The low pH and temperature help to limit overoxidation of the polyaniline which is formed. Nevertheless, the insolubility of the product in the reaction solution promotes crosslinking between polymers by the strong oxidant. Consequently the solubility and electrical conductivity of the product may not be optimized. Use of a weaker oxidant may enable the synthesis of more linear and conductive polyaniline emeraldine acid salts.

Genies and co-workers found that under strong oxidative conditions ortho-substitution, yielding phenazine units, occurs along the polyaniline backbone. The phenazine unit has been associated with the "middle peak" in the polyaniline cyclic voltammogram which occurs at about 0.45 versus Cu/CuF_2. The phenazine peak is not formed, however, if lesser oxidizing conditions are used. The phenazine impurity is expected to reduce the conductivity and solubility of the polyaniline product.

A comparison of cyclic voltammograms of polyaniline synthesized electrochemically by step-cycling to 0.8V versus SCE with that of polyaniline synthesized via the common oxidative polymerization of aniline in aqueous hydrochloric acid using ammonium peroxydisulphate shows more crosslinking occurs in the chemically synthesized product. Obviously polyaniline made via this method is not optimized with respect to electrical conductivity and solubility. Use of a milder oxidant than ammonium peroxydisulphate may moderate crosslinking. Unfortunately, aniline requires a strong oxidant to achieve oxidation with consequent polymerization.

One method of lowering the oxidation potential needed to synthesize polyaniline is to start with an electron rich aniline oligomer, rather than aniline. For example, n-phenyl-p-phenylenediamine (p-dianiline) has an oxidation potential at 0.45 versus SCE. Conductive polyaniline emeraldine is stable at this potential. If p-dianiline undergoes polymerization upon oxidation at this potential, over-oxidation of the polyaniline emeraldine to higher oxidative and less conductive states may not occur, and crosslinking may be limited.

Unfortunately, p-dianiline is not found to efficiently polymerize upon oxidation. When cycled to 0.6 V versus SCE, well above the oxidation potential of p-dianiline, no polyaniline is seen to form after 200 step cycles. Although the p-dianiline is found to undergo a fast electron transfer during oxidation, the oxidized product is not found to efficiently undergo further chemical reaction. These results show that although the n-phenyl-p-phenylenediamine is easily oxidized at potentials lower than aniline oxidation, the aniline dimer does not efficiently polymerize to polyaniline emeraldine.

Aniline is inefficient at undergoing oxidation at potentials at which the product polyaniline emeraldine is stable. N-phenyl-p-phenylenediamine, although undergoing oxidation at these lower potentials, does not efficiently undergo polymerization. However a mixture of aniline and n-phenyl-p-phenylenediamine is found to undergo polymerization to polyaniline at low potentials. Only a small amount of p-dianiline in an acidic aniline solution is needed to allow polyaniline formation.

Even if only cycled to 0.45V versus SCE, polyaniline is found to form from a 10:1 mixture (by weight) of aniline and p-dianiline. The polyaniline product shows little evidence of crosslinking. A CV of this polyaniline product taken in an acid solution with no aniline or p-dianiline present, shows no peak at 0.45V versus SCE.

A mechanism which explains this phenomenon has been postulated. The p-dianiline is oxidized at the low potential. This oxidized species is long lived enough to undergo coupling with unoxidized aniline. Further oxidation and coupling with unoxidized aniline occurs until polyaniline emeraldine is formed.

This study reveals a method by which polyaniline can be synthesized using mild oxidants in order to avoid overoxidation and or crosslinking of the product. Improved solubility and electrical conductivity of the product is expected using this method. P-dianiline may also prove to be useful in improving the kinetics of polyaniline formation during ammonium peroxydisulfate oxidation of aniline. Consequently higher yields may be possible.

Anhyride Derivatized Polyaniline Emeraldine

Processability and thermal stability of conductive polymers is essential for these materials to be useful. As part of Lockheed's internal research program on conductive polymers, we discovered that polyaniline emeraldine free-base can be derivatized to its electrically conducting state by either carbonic or sulfonic anhydrides. The resulting conductive polymer is soluble in organic solvents such as n-methyl(pyrrolidinone) (NMP). For example, tosylic anhydride is found to be soluble in NMP although the corresponding PANFB derivatized with tosylic acid is insoluble. The large tosyl groups help to solubilize the polymer in less polar media.

This type of polyaniline derivatization opens up potential for various processing methods. For example, blending of the conductive polymer with other soluble polymers is made possible. As part of our URI project, we have studied the basic properties of anhydride derivatized polyaniline. Of particular importance is the affect of the amide or sulfonamide bond on the properties of polyaniline.

One important topic is the electrical conductivity of the polyaniline derivatized with dianhydrides. We have found that the electrical conductivity of polyaniline is strongly dependant on the anhydride used, for example the sulfonic anhydride derivatized polyaniline is generally found to be more conductive than the carbonic anhydrides. This is probably due to the stronger electron withdrawing nature of the sulfonyl group than the carbonyl group.

These materials were synthesized in a dry-box under Argon to eliminate any possibility of anhydride hydrolysis to form the corresponding protonic acid. The anhydride and polyaniline emeraldine free-base were mixed in NMP and stirred for 12 hours. The derivatization could be altered by varying the amount of anhydride used. The green solution was then dripped into toluene to precipitate the conductive polymer. The precipitate was then washed with hexane under argon. After heating at 100 degrees celsius for 10 minutes to remove excess solvent, the green powder was then pressed into a pellet for conductivity measurements.

An important factor in determining the utility of these materials is their thermal stability. We have found anhydride derivatized polyaniline to be stable, however, this stability is strongly dependant on the extent to which the polyaniline is derivatized. For example if a sample of polyaniline in which there exists one tosylic anhydride for every eight aniline units along the polyaniline backbone is heated at 200 degrees celsius for one hour, only a slight decrease in conductivity is seen. However, a sample in which there exists one tosylic

anhydride molecule for every aniline unit, decomposes quickly when heated at 200 degrees celsius for one hour. Although the exact amount of anhydrides bound to the polyaniline backbone as well as their specific binding sites could not be completely controlled, this does reveal that excess tosylic anhydride does destabilize the polyaniline.

The same phenomenon occurs with carbonic anhydrides, but to a greater extent. The carbonic anhydride does not stabilize polaron separation as well on the polyaniline backbone. However, the carbonyl group is more reactive with amines than the sulfonyl group, due to less steric hindrance. Consequently the carbonic anhydrides can quickly react with an excessive percentage of the polyaniline amines, which leads to decomposition of the polymer. For example, if excess acetic anhydride is mixed with polyaniline free-base in NMP, the blue polyaniline emeraldine free-base turns red, without going through a green conductive state. This suggests that the acetic anhydride reacts with the polyaniline backbone, withdrawing a significant amount of electron density from it, without stabilizing polaron separation. Larger carbonic anhydrides such as butanoic anhydride or benzoic anhydride decompose the polyaniline less quickly.

Tosylic anhydride probably renders the polyaniline conductive by binding to its amine groups. This is analogous to the Bronsted Acid doping of polyaniline emeraldine free-base to its conductive state. Excessive doping of polyaniline by Bronsted Acids has not been seen to lead to a decrease in the polyanilines conductivity. In other words, when doping polyaniline emeraldine free-base with protonic acids, the conductivity is only seen to increase as the doping level is increased.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

Summary of Progress

The results of our collaborative study with the University of Lowell on the placement of defects in polyacetylene was published in August (Clough et al., Makromol. Chem. Rapid. Commun., 9, 535, 1988). The paper outlines reasons why defect placement should not be random based on thermodynamic considerations and explains why the optical absorption spectra of "segmented" polyacetylenes are inconsistent with short conjugated segments. We consider this to be a major contribution to our understanding of defect placement. Also, our work suggests that a significant amount of chemical modification (e.g., functionalization) of polyacetylene can be tolerated without major compromises in electrical properties.

The results of our efforts in this area cause us to question recent reports on the unusually high conductivity (ca. 10^{-1} S/cm) observed upon doping cis-1,4-polyisoprene (PI) with iodine. PI is not conjugated, having double bonds flanked by two methylenes. Iodine is simply not a strong enough oxidant to generate a radical cation from an isolated double bond, and there is no precedence in the literature for such a reaction with small-molecule olefins. The reason for the high observed conductivity is not clear - it may be the result of extensive chemical modification (iodination followed by dehydroiodination to yield iodo-substituted *polyacetylenes*), or ion transport. We have treated PI with iodine and achieved conductivities of ca. 10^{-2} S/cm, close to the reported values. Conductivities of 10^{-6} S/cm are observed for cis-1,4-polybutadiene (PB) treated with iodine, even though earlier reports claimed that virtually no change in conductivity occurs with iodine doping. Also, an earlier suggestion that the higher conductivity of I_2-treated PI vs. PB was due to the presence of electron-donating methyls in the former. This notion is discredited by our observation that cis-polychloroprene also attains a conductivity of ca. 10^{-6} S/cm on exposure to iodine, even though the double bonds in this material contain *electron-withdrawing* chlorines. Clearly, these observations require a major reinterpretation of the mechanism of carrier generation and transport in non-conjugated polymers, and this remains as a subject of continuing study in our laboratory.

We have prepared polypyrrole-poly(styrene sulfonate) [PP/PPS] composites by the method of Miller and coworkers to determine the ability of such materials to reversibly bind and release proteins and other biological macromolecules. Our interest is motivated by the possibility of using these electroactive polymers in AIDS therapy, as it has been shown recently that dextran sulfate (a polyanion) is one of the more promising agent for the inhibition of infectivity of HIV. Controlled release of polyanions or binding of virus particles containing cationic coat proteins (as does HIV) is of particular interest. Our initial experiments have focused on the ability of PP/PSS to bind cationic proteins known as histones. While our first experiments showed that in phosphate buffer film is not very stable, apparently due to nucleophilic attack by phosphate on the oxidized PP, this problem has been circumvented by employing TRIS buffer. Attempts to bind histone by PP/PSS as PP is reduced electrochemically have failed because the histone has a high affinity for PSS and actually removes PSS from the film. This is exactly the opposite of the desired result, and indicates to us that the sulfonates need to be covalently fixed to the PP in order to afford histone binding at the electrode. Experiments of this nature are underway.

5. University of Rhode Island

Department of Chemistry (Yang)

Summary of Progress

The most interesting development in this quarter is that we have observed an additional absorption band at 0.6 eV for the conductive form of polyaniline. The band intensity of this new band changes as a function of the applied potential and it is synchronized with the evolution of the 2.9 eV, 1.5 eV and 1.0 eV bands.

We observe the 0.6 eV absorption band for a polyaniline film electrochemically formed on fluoride doped tin oxide glass (NESA) and immersed in pH 1 electrolyte solution. The intensity of the 0.6 eV band increases as the potential is increased from -0.4 V to +0.4 V vs. SCE, and decreases as the potential is increased from 0.4 V to 0.7 V.

The corresponding changes of the same polyaniline sample in the visible absorption region shows the spectrum is noisy for the frequency range lower than 4000/cm so the position of the absorption maximum of the 0.6 eV band is not clearly defined. But from data we obtained so far there appears to have a maximum between 5000/cm and 4000cm. We also observe another absorption band at 1 eV which has very similar characteristics as the 0.9 eV band that we observed previously. Both bands are due to polyaniline. The substrate tin oxide does not exhibit electrochromism under these experimental conditions.

We now found two types of near IR absorption: In type A sample a 0.9 eV band was found for polyaniline coated on tin oxide glass from one supplier. In type B sample, two near infrared bands at 0.6 and 1.0 eV are observed for tin oxide glass made by a different supplier. We know that the tin oxide coating for type B sample was doped with fluorides. We do not know the composition of the tin oxide coating for type A samples yet.

The substrate dependence of the absorption spectrum is reproducible. The absorption spectra are definitively dependent on the substrate.

What is the nature of these absorption transitions? There are several possibilities. We are currently studying the kinetics of the switching process to see if we can distinguish them.

Other part of our research concerns the building of the electrochemical-optical-EPR apparatus. We have started with the construction of fiber optics

adapter for an optical spectrometer belonging to the chemistry department. Originally we had proposed to purchase a dedicated spectrometer for this purpose. It is not possible now because of insufficient funds. The progress in this part of the project is considerably slower than what we would like to see because of the limited access to the departmental spectrometer.

6. Montclair State College

Department of Chemistry (Humphrey)‡

Summary of Progress

A novel method of synthesizing the conducting polymer polyaniline in film form was investigated. Films were varied in thickness from 1 to 10 mils and were characterized in both the conducting and insulating form. Several different methods were attempted in order to achieve uniform doping of the polymer films, however different dopant acids yielded different results using different methods and no single doping method could be isolated as being the best.

In general, the films were formed by dissolving the emeraldine base form of polyaniline in an organic solvent such as n-methylpyrrolidone (NMP), casting the polymer solution on pyrex plates then evaporating the solvent in a well ventilated oven at 82°C. The resulting polyaniline base films (nonconducting) could be peeled from the pyrex as a sheet. These films could then be doped with acids such as hydrochloric acid, dodecylbenzene sulfonate, methyl sulfonic acid, nitric acid, sulfuric acid, benzene sulfonic acid, and toluene sulfonic acid.

These polymer films were subjected to a wide range of tests. For example, mechanical testing (stress-strain curves), electrochemical characterization (cyclic voltammetry), and spectroscopic characterization (Fourier transform infrared spectroscopy).

‡Research carried o ıt collaboratively with the Naval Air Development Center in Warminster, PA.

III. Working Relationships Involving University of Pennsylvania Personnel and Those of Subcontractors

The following interactions between personnel funded by the URI contract have taken place during this quarter:

August 6-20, 1988, Mr. Jiang Yue from the Ohio State University visited Dr. MacDiarmid's group to learn electrochemical preparation techniques of polyaniline.

August 23-24, 1988, Dr. Randy Cameron from the URI group at Lockheed in Burbank, California visited Ohio State and presented a talk on current interests of Lockheed pertaining to polyaniline and discussed joint URI collaborative research. He also visited Dr. MacDiarmid's laboratory on August 26, 1988. Title of talk given: "New Synthetic Routes of Polyaniline."

August 25-29, 1988, Dr. Nicolas Theophilou from the University of Pennsylvania visited Ohio State to perform joint experiments on highly-conducting polyacetylene and presented several related lectures.

August 29 - September 2, 1988, Mr. Mikolaj Jozefowicz from Ohio State visited Dr. McDiarmid's group at the University of Pennsylvania to discuss the chemistry and preparation of polyaniline.

September 8-9, 1988, Dr. MacDiarmid visited Ohio State University to discuss joint URI collaborative research.

September 22-25, 1988, Mr. Sanjeev Manohar from the University of Pennsylvania visited Ohio State to discuss new developments in preparation of polyaniline and participated in joint research.

IV. Miscellaneous Scientific Interactions of Key Personnel Associated with the Program involving (i) visits to their laboratories by persons concerned with conducting polymers, (ii) visits by them to other laboratories and (iii) lectures on their research at organized symposia.

1. July 2, 1988, Dr. Epstein met in Santa Fe, NM with Professor Anvar Zakhidov of the USSR Academy of Sciences and Professor Siegmar Roth of the Max Planck Institute to discuss future research directions on conducting polymers in Europe and the Soviet Union.

2. July 5, 1988, Dr. Olivier Sagnes, Thomson-CSF, Central Research Laboratories, Orsay, France visited Dr. Epstein's laboratory. He discussed microwave properties of conducting polymers.

3. July 6, 1988, Dr. Toshiyuki Ohsawa and Dr. Miyata of Ricoh Company Ltd., Japan visited Dr. MacDiarmid's laboratory to discuss research in the conducting polymer field.

4. July 6, 1988, Dr. Claude Mathis of Institute of Straasborg, France visited Dr. MacDiarmid's Laboratory to discuss research in the conducting polymer field.

5. July 7, 1988, Drs. M. Galtier, A. Montaner and J. L. Sauvajol of Montpellier, Cedex, France visited Dr. MacDiarmid's laboratory. Title of talk given: "Spectroscopic Studies in Polythiophene."

6. July 7-21, 1988, Mr. Pascal Franchept of the University of Nantes, Cedex, France visited Dr. MacDiarmid's laboratory to learn the synthesis and characterization of conducting polymers.

7. July 8, 1988, Dr. Steve Armes of Los Alamos National Laboratories visited Dr. Tim Obey and Dr. MacDiarmid at Dr. MacDiarmid's laboratory. Title of the talk given: "Colloidal Forms of Conducting Polymers."

8. July 8-15, 1988, Professor Eitan Ehrenfreund, Technion-Israel Institute of Technology, Haifa, Israel visited Dr. Epstein's laboratory. He discussed the optical response and the insulator-metal transition in conducting polymers.

9. July 9-10, 1988, Professor Adam Pron, University of Warsaw, Warsaw, Poland visited Dr. Epstein's laboratory. He discussed doping mechanisms in conducting polymers and Mösbauer spectroscopy.

10. July 11-15, 1988, Dr. Adam Pron of the University of Warsaw, Poland visited Dr. MacDiarmid's laboratory. Title of the talk given: "Mösbauer Spectroscopic Studies of Selected Conducting Polymers."

11. July 14, 1988, Dr. Brian Saville of Courtaulds Research, London, England visited Dr. MacDiarmid's laboratory. Title of talk given: "Technology of Power Coating and Compounds Exhibiting Photochromism."

12. July 14, 1988, Dr. Serdar Sariciftci of the University of Vienna, Austria visited Dr. MacDiarmid's laboratory. Title of talk given: "Spectroscopic Studies on Doping of Polyanilines."

13. July 18-23, 1988, Dr. G.C. Farrington attended the Asian Workshop on Solid State Ionics at Singapore. Title of the invited talk: "Solid State Electrochemistry and Polymer Electrochemistry."

14. July 19-20, 1988, Dr. N. Serdar Sariciftci of the University of Vienna, Austria visited Dr. Epstein's laboratory. Title of talk given: "Spectroscopic Studies of the Properties of Polyaniline."

15. July 22, 1988, Dr. A.G. MacDiarmid attended the Presidential Conference on Chemistry in the Museum Environment, Philadelphia, PA. Title of invited lecture: "Conducting Polymers."

16. July 25-28, 1988, Dr. G.C. Farrington attended the China Workshop on Solid State Ionics at Day-Ong, People's Republic of China. Title of invited talk: "Solid State Electrochemistry and Polymer Electrochemistry."

17. July 25-29, 1988, Dr. Epstein attended the International Conference on Magnetism in Paris, France. This trip was not supported by URI funds.

18. July 25-29, 1988, Dr. A.G. MacDiarmid attended the Gordon Research Conference on "Solid State Chemistry," Plymouth, NH. Title of invited lecture: "Organic Semiconductors and Metals."

19. July 25-August 5, 1988, Dr. Epstein performed collaborative studies with Professor Jean-Paul Pouget at the Universite Paris-Sud in Orsay, France on the crystal structure of polyanilines.

20. July 26, 1988, Dr. Vlado Tabacik of the University of Montpellier, France visited Dr. MacDiarmid's laboratory to discuss research in the conducting polymer field.

21. July 27, 1988, Dr. Patrick Bernier of the University of Montpellier, France visited Dr. MacDiarmid's laboratory. Title of talk given: "Staging During Electrochemical Doping of $(CH)_x$ with Alkali Metals."

22. July 28, 1988, Dr. H. Tomozawa of the Institute of Polymer and Organic Solid, University of California, Santa Barbara, CA visited Dr. MacDiarmid's Laboratory. Title of talk given: "Metal Polymer Schottky Barriers on Cast Films of Soluble Poly(3-Alkyl Thiophenes)."

23. August 8-12, 1988, Dr. A.G. MacDiarmid attended the Gordon Research Conference on "Electron Donor Acceptor Interactions," Wolfeboro, NH. Title of invited lecture, "Polyaniline: A New Concept in Conducting Polymers."

24. August 9-10, 1988, Dr. H. Tomozawa, University of California, Santa Barbara, CA visited Dr. Epstein's laboratory. Title of talk given: "Metal/Polymer Schottky Barriers on Soluble Poly(3-hexylthiophene)."

25. August 10, 1988, Dr. Epstein met in Cambridge, UK with Professor Richard Friend of the Cavendish Laboratory to discuss optical response on conducting polymers and the fabrication of electronic devices from conducting polymers.

26. August 15, 1988, Dr. Hans Kuhn of Milliken Research Corporation, Spartanburg, SC visited Dr. MacDiarmid's laboratory. Title of talk given: "Conductive Textiles."

27. August 21-22, 1988, Dr. A.G. MacDiarmid visited the IBM Research Center at York Town Heights, NY. Title of invited lecture, "Synthetic Metals: A New Role for Organic Polymers."

28. August 22-24, 1988, Dr. Brian Vincent of the University of Bristol, London, England met and held discussions with Dr. Barbara Schneider and Dr. MacDiarmid at Dr. MacDiarmid's laboratory regarding biomedical applications of conducting polymers.

29. August 31-September 2, 1988, Dr. Esther Conwell of Xerox Webster Research Center, Webster, NY visited Dr. Epstein's laboratory. Title of talk given: "Insulator-Metal Transition in Polyacetylene and Photoconductivity in Polyacetylene."

30. September 15-16, 1988, Dr. Epstein visited DuPont de Nemours in Wilmington, DE to discuss joint conducting polymer processing research.

31. September 15-October 10, 1988, Mr. Mikolaj Jozefowicz met in Orsay, France with Professor J.P. Pouget to perform crystal structure studies on the polyanilines.

32. September 16-24, 1988, Dr. MacDiarmid's visit to France at the invitation of the Ministry of Defense included several invited lectures:

(i) 9/19 - A general talk at the Ministry of Defense, "Conducting Polymers" and a second lecture on "Electronically Conducting Polymers: Past, Present and Future."

(ii) 9/20 - University of Grenoble, invited lecture "Electronic Conducting Polymers."

(iii) 9/21 - At CNRS, Thiais, invited lecture "Electronically Conducting Polymers: Past, Present and Future."

(iv) 9/22 - At University of Nantes, invited lecture "Electronically Conducting Polymers: Past, Present and Future."

33. September 26-30, 1988, Dr. Richard McCall of the Ohio State University, attended a training course at Nicolet Instruments in Madison, WI and discussed applications of FTIR spectroscopy.

V. Publications

1. Papers Published

Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Conduction Mechanism of Polyaniline: Effect of Moisture," Synth. Met., 26, 1 (1988), H.H.S. Javadi, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Solid-State ^{13}C NMR Characterization of Polyanilines." J. Am. Chem. Soc., 110, 7647 (1988), S. Kaplan, E.M. Conwell, A.F. Richter and A.G. MacDiarmid. (Supported in part by URI and in part by Xerox Corporation).

(ii) Wnek (RPI)

"A Comment on Random Versus Non-Random Defect Placement in Polyacetylene," Makromol. Chem. Rapid. Commun., 9, 535 (1988). S. Clough, S. Tripathy, X. Sun, B. Orchard and G. Wnek. (Supported in part by URI and in part by an ONR contract to S.T.)

"Conduction Mechanisms in Polyaniline (Emeraldine Salt)." J. Electroanal. Chem. 256, 343 (1988). W.W. Focke and G.E. Wnek. (Supported in part by URI and a fellowship from the Council for Scientific Research of South Africa).

2. Papers Accepted/Submitted for Publication

(a) Acknowledging URI Support Only

(i) Kuan (Lockheed)

"The Effect of N-Phenyl-P-Phenylenediamine On the Electro-Polymerization of Aniline," J. Electro. Chem. Soc., submitted (1988), S.K. Preto Clement and R.E. Cameron.

(b) Acknowledging URI and Other Support

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Microwave Transport in the Emeraldine Form of Polyaniline," Phys. Rev. B, submitted (1988), H.H.S. Javadi, F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"AC Conductivity of Emeraldine Polymer," Phys. Rev. B, in press (1988), F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Massive Polarons In Large-Gap Polymers," Phys. Rev. B, submitted (1988), R.P. McCall, J.M. Ginder, M.G. Roe, G.E. Asturias, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"The Polyanilines: Processing, Molecular Weight, Oxidation State and Derivatives," Polymer Preprints, submitted (1988), A.G. MacDiarmid, G.E. Asturias, D.L. Kershner, S.K. Manohar, A. Ray, E.M. Scherr, Y. Sun, X. Tang and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059 and in part by University of Pennsylvania).

(ii) Farrington (Penn)

"Studies of the Hydration of Transition Metal Cations Dissolved in Poly(ethylene oxide) by UV/Visible Spectroscopy," J. Electrochem. Soc., in press (1988), R. Huq, M.A. Saltzberg and G.C. Farrington. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059.)

(iii) Kuan (Lockheed)

"Electrochemical and Chemical Studies of the Oxidative Polymerization of Aniline: Coupling of Aniline with Oxidized N-Phenyl-P-Phenylenediamine," Synth. Met. submitted (1988), R.E. Cameron, S.K. Clement. (Supported in part by URI and in part by Lockheed Corporation).

(iv) Wnek and MacDiarmid (RPI/Penn)

"Synthesis and Electrochemistry of Alkyl Ring Substituted Polyaniline." Y. Wei, W.W. Focke, G.E. Wnek, A. Ray and A.G. MacDiarmid, J. Phys. Chem., in press (1988). (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

VI. Patents

Patents resulting from URI support

None

VII. Changes in Personnel

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)

Two second year graduate students, Xun Tang and Yan Sun, were added to the URI grant, effective July 1, 1988. One quarter of their salary and tuition is being paid by the URI grant.

In addition, two students were hired for the summer on July 1, 1988 as lab technicians: Nicholas Cawdery, of the University of Bristol, England, and Debora Schwartz, an undergraduate chemistry major at Penn. Nicholas Cawdery resigned on September 9, 1988 and Debora Schwartz on August 31, 1988.

Dr. K. V. Ramanathan, whose 50% salary was paid by Dr. MacDiarmid's URI Grant, resigned on September 29, 1988 and returned to the Indian Institute of Science, Bangalore to continue as a member of the faculty.

b. Department of Materials Science and Engineering (Farrington)

There were no changes in personnel during this quarter.

2. The Ohio State University

Department of Physics (Epstein)

Mr. John Ginder began employment as a Postdoctoral Research Associate on July 1, 1988. Ms. Hong-Juan Ye began employment as a Research Aid on August 1, 1988. Mr. Zhaohui Wang began employment as a Graduate Research Associate on July 1, 1988.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

There were no changes in personnel during this quarter.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

There were no changes in personnel during this quarter.

5. University of Rhode Island

Department of Chemistry (Yang)

There were no changes in personnel during this quarter.

6. Montclair State College

Department of Chemistry (Humphrey)

There were no changes in personnel during this quarter.

VIII. Contractual Administration

1. Prime Contract - University of Pennsylvania (MacDiarmid)

All funding for the second year (i.e. 10/1/87 to 9/30/88) was received by the University of Pennsylvania, Office of Research Administration in the following increments: February 17, 1988, $500,000; June 28, 1988, $1,008,000, bringing the total amount for the second year to $1,508,000.

2. Subcontractors

The modifications have been approved or are in the process of being approved by the corresponding institutions as noted below:

a. Ohio State University (Epstein)

(i) Amendments to subcontract mailed by Ms. Sandra Houck of the Office of Research Administration at the University of Pennsylvania to OSU on 6/28/88. Modifications include an extended performance period to 3/30/89 and an increase in funds available to subcontractor to $1,236,713.00.

(ii) Fully executed copy of amendment received from OSU on July 6, 1988.

b. Lockheed Corporation (Kuan)

(i) Amendment to subcontract mailed by Ms. Sandra Houck of the Office of Research Administration at the University of Pennsylvania to Lockheed Corporaton on 7/27/88. Modifications include an extended performance period to 3/30/89 and an increase in funds available to subcontractor to $174,074.00.

(ii) Fully executed copy of amendment not yet received from Lockheed corporaton as of 9/15/88. Another copy of amendment is being mailed by Ms. Sandra Houck of the Office of Administration at the University of Pennsylvania. The first copy was lost in the mail.

c. Rensselaer Polytechnic Institute (Wnek)

(i) Amendment to subcontract mailed by Ms. Sandra Houck of the Office of Research Administration at the University of Pennsylvania to Rensselaer Polytechnic Institute on 6/27/88. Modifications include an extended performance period to 3/30/89 and an increase in funds available to subcontractor to $105,946.00.

(ii) Fully executed copy of amendment received from Rensselaer on 9/9/88.

d. The University of Rhode Island (Yang)

(i) Amendment to subcontract mailed by Ms. Sandra Houck of the Office of Research Administration at the University of Pennsylvania to The University of Rhode Island on 6/28/88. Modifications include an extended performance period to 3/31/89 and an increase in funds available to subcontractor to $63,724.00.

(ii) Fully executed copy of amendment received from University of Rhode Island on 7/28/88.

e. Montclair State College (Humphrey)

(i) Amendment to subcontract mailed by Ms. Sandra Houck of the Office of Research Administration at the University of Pennsylvania to Montclair State College on 6/28/88. Modifications include an extended performance period to 3/31/89 and an increase in funds available to subcontractor to $61,093.00.

(ii) Fully executed copy of amendment received from Montclair State College on 7/28/88.

f. Macgill Management, Inc. (Dolton)

(i) Amendment to subcontract mailed by Ms. Sandra Houck of the Office of Research Administration at the University of Pennsylvania to Macgill Management, Inc. on 6/23/88. Modifications include an extended performance period to 3/31/89 and an increase in funds available to subcontractor to $67,389.00.

(ii) Fully executed copy of amendment received from Macgill Management, Inc. on 7/13/88.

IX. Fiscal Status
Expenditures and Commitments

A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.

	1 1st Year Budgeted 9/15/86-9/30/87	2 2nd Year Budgeted 10/1/87-9/30/88	3 New Funding added on 2/17/88 & 6/28/88	4 Total Spent & Committed 9/15/86-9/30/88	5 Available Balance on 9/30/88	6 Budgeted Balance
U of P (Chem) (Dr. A.G. MacDiarmid)	727,044	577,611	187,466 + 390,145 = 577,611	1,123,234	181,421	181,421‡
U of P (MSE) (Dr. G.C. Farrington)	231,565	309,845	102,108 + 207,737 = 309,845	541,410	0	0

‡Available balance for MacDiarmid and Farrington consists entirely of unexpended equipment monies. These funds must be used for salaries and supplies until we have received funds for the third year budget.

B. Subcontracts

	1st Year Budgeted 9/15/86-9/30/87	2nd Year Budgeted 10/1/87-9/30/88	New Funding added on 2/17/88 & 6/28/88	Total* Spent & Committed 9/15/86-9/30/88	Available Balance on 9/30/88 (1+3)-4	Budgeted Balance (1+2)-4
OSU (Dr. A.J. Epstein)	867,116	369,597	121,800 + 247,797 = 369,597	1,197,013	39,700	39,700
Lockheed (Dr. T. Kuan)	87,037	87,037	30,732 + 56,305 = 87,037	135,747	38,327	38,327
MM Inc. (Ms. M. Dolton	37,143	30,246	11,985 + 18,261 = 30,246	67,389	0	0
Academic Subcontrators						
a. Dr. G.E. Wnek						
1. MIT	36,996	0	0	36,796	200	200
2. RPI	36,006	69,940	31,862 + 38,078 = 69,940	73,593	32,353	32,353
b. Univ. Rhode Island (Dr. S. Yang)	31,862	31,862	31,862 = 31,862	55,072	8,652	8,652
c. Montclair State (Dr. B. Humphrey)	29,231	31,862	14,047 + 17,815 = 31,862	45,462	15,631	15,631

*The following represents monies paid on receipt of demand (i.e., bills) from participating subcontracts.